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# Concentration of Li atoms in plasmas produced from laser ablation of LiNbO<sub>3</sub>

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An analytic kinetic model capable to predict the spatial and temporal evolution of the population densities of ground and excited state Li atoms (up to the  $3^2D$  level) in nonequilibrium laser-generated plasmas from LiNbO<sub>3</sub> targets is presented. The model is especially useful as a nonequilibrium diagnostic tool for determining the concentrations of Li atoms from available measurements of electron density ( $N_e$ ) and temperature ( $T_e$ ). In addition, the present approach is able to determine the electron kinetic mechanisms contributing to populate and depopulate the Li atom ground and excited states in laser-produced plasmas. A very reasonable qualitative agreement is found when comparing the model predicted Li atom densities with those obtained experimentally. Thus, the proposed approach can be used as a useful tool to optimize the processes involved in pulsed laser deposition of LiNbO<sub>3</sub> thin films. © 2001 American Institute of Physics. [DOI: 10.1063/1.1381553]

## I. INTRODUCTION

Lithium niobate (LiNbO<sub>3</sub>) is a well-known material with excellent nonlinear properties of interest for piezoelectric and electro-optic applications.<sup>1</sup> However, although pulsed laser deposition (PLD) has proven to be one of the most successful techniques in growing complex oxide materials, low Li-content LiNbO<sub>3</sub> films remain the main problem when using PLD. While some recent works have appeared so far to explain this Li deficiencies, very few of them have focused on the study of key plasma parameters, such as, for instance, the electron density and electron temperature or the kinetic mechanisms influencing the spatial and temporal evolution of the population density of Li atoms present in the plasma plume.

Therefore, the main goal of this work is to build a collisional-radiative kinetic model of the nonequilibrium lithium-like plasmas generated from the laser ablation of LiNbO<sub>3</sub> targets. Such a kinetic model is a valuable tool that will provide us with complementary information to that obtained experimentally and it will help to have a better understanding of how the properties of the plasma produced in the PLD process influence the properties of the synthesized LiNbO<sub>3</sub> thin films. In order to achieve this objective, I have modified the basic diagnostic method set up by Suckewer<sup>2</sup> and Kunc<sup>3</sup> for lithium-like ions by substituting the electron-ion rates by the very accurate electron-atom collisional rates proposed by Kunc and Zgorzelski<sup>4</sup> using suitable electron-impact atom excitation cross sections based on the classical binary-encounter theory by Gryzinski.<sup>5</sup>

The laser-generated plasma from the ablation of LiNbO<sub>3</sub> targets is mainly composed of Nb atoms, O atoms, O<sub>2</sub> molecules, possibly some NbO and LiO molecules and, due to its low ionization and excitation energy thresholds, Li<sup>+</sup> and Li atoms in their ground and several excited levels. However,

in this work I focused my attention in the kinetics of Li atoms.

The present approach allows one to determine the spatial and temporal evolution of the concentrations of Li atoms in plasmas produced from pulsed laser ablation of LiNbO<sub>3</sub> targets in vacuum by simply introducing the measured  $N_e$  and  $T_e$  values into the model equations.

Therefore, the collisional-radiative model presented here can be used as a useful diagnostic tool for determining not only the ground and several excited Li atom population densities, but also to estimate the deviation of the laser-produced plasma from thermodynamic equilibrium as well as the spatial and temporal evolution of electron-impact rate coefficients and the relaxation times of all the considered Li atom levels.

## II. KINETIC MODEL

In a plasma, where atom-atom inelastic collisions and particle diffusion are neglected, the net production of excited atoms can be determined by balancing all collisional and radiative processes populating and depopulating each atomic level. Thus, in my case, the net production rates of Li atoms excited to the  $i$ th level and of plasma electrons can be given, respectively, by<sup>6</sup>

$$\begin{aligned} \frac{\partial N_i}{\partial t} = & \sum_{j < i} N_e N_j C_{ji} + \sum_{j > i} N_e N_j R_{ji} + \sum_{j > i} N_j A_{ji} \kappa_{ji} \\ & + N_e^2 N^+ \beta_{ci} - N_i \left( \sum_{j > i} N_e C_{ij} + \sum_{j < i} N_e R_{ij} \right. \\ & \left. + \sum_{j < i} A_{ij} \kappa_{ij} + N_e S_{ic} \right) \end{aligned} \quad (1)$$

and

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$$\frac{\partial N_e}{\partial t} = N_e N_1 S_{1c} - N_e^3 \beta_{c1}, \quad (2)$$

where  $N_{i,i \neq 1}$  and  $N_1$  are the population densities of, respectively, the excited and ground Li atoms, and  $N_e$  and  $N^+ \approx N_e$  are, respectively, the concentrations of electrons and of all the possible positive ions present in the plasma (not only those of Li) in their ground energy level (for the sake of simplicity, I have only considered ground state ions);  $C_{ij}$  is the rate coefficient for electron-impact excitation of the  $j$ th atomic level from the lower level  $i$ ;  $R_{ji}$  is the rate coefficient for electron-impact deexcitation of level  $j$  into a lower level  $i$ ;  $S_{ic}$  is the rate coefficient for ionizing collisions of an electron with an atom in its ground or excited level  $i$ ;  $\beta_{ci}$  is the rate coefficient for three-body recombination producing an atom excited to the  $i$ th level;  $A_{ji}$  is the transition probability for  $j \rightarrow i$  spontaneous emission, and  $\kappa_{ji}$  is a radiation escape factor for the radiation emitted in bound-bound transitions in the plasma.

The considered rate equations are linear with respect to both the ground and excited Li atom population densities, and  $N_e$  and  $T_e$  are taken as input parameters of the model. The linearity of the model equations is a consequence of two approximations: (i) atom-atom inelastic collisions are neglected so that the Li atom concentrations are controlled by electron-atom collisions and radiative transitions, and (ii) the reabsorption of plasma radiation by Li atoms is represented by radiation escape factors which are taken as constant parameters in the rate equations. This radiation escape factors have the same physical meaning as those introduced by Holstein,<sup>7</sup> that is, they take into account the reabsorption of radiation in such a way that the quantity  $N_j A_{ji} \kappa_{ji}$  represents the net radiation produced in the  $j \rightarrow i$  transition. The factor  $\kappa_{ji}$  changes from one (when the plasma is optically thin for the  $j \rightarrow i$  radiation) to zero (when the radiation from the transition  $j \rightarrow i$  is completely reabsorbed in the plasma). In my case, I have assumed that the plasma is optically thin ( $\kappa_{ji} = 1$ ) for all the dipole-allowed radiative transitions considered. In order to study the kinetics of lithium atoms and ions, I need to consider their basic energy level structure. I show in Fig. 1 a diagram corresponding to the five lower energy levels (up to the  $3^2D$  level corresponding to  $\sim 4$  eV) of the Li atom including the continuum of energy (from 5.4 eV). The electric dipole-allowed transition probabilities<sup>8</sup> and the statistical weights of the energy levels considered are also indicated in Fig. 1 (see also Table I).

The collisional-radiative scheme proposed by Suckewer<sup>2</sup> incorporating the improvements suggested by Kunc<sup>3</sup> is sketched out later. The application of such a kinetic model to the study of the plasma generated by laser ablation of a LiNbO<sub>3</sub> target gives very useful expressions for the population densities of the ground and excited Li atoms detected in the nonequilibrium laser produced plasma present in PLD processes. If I rewrite Eq. (1) for the case of steady-state plasmas I find,<sup>2,3</sup>

$$N_i \left( \sum_{j < i} A_{ij} \kappa_{ij} + N_e \sum_{j < i} R_{ij} \right) = \sum_{j < i} N_e N_j C_{ji} + \delta, \quad (3)$$

where

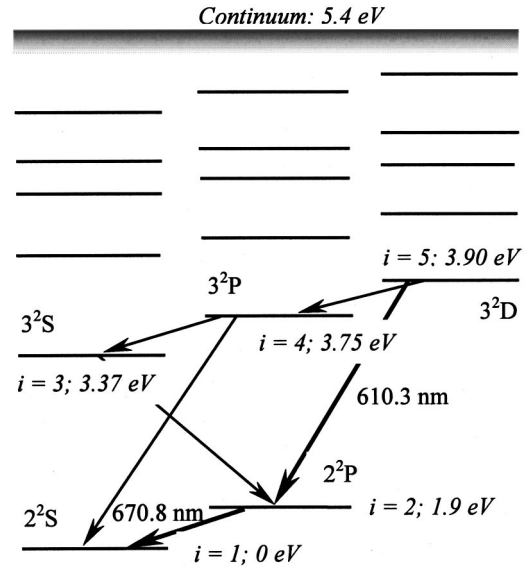


FIG. 1. Diagram of the lower energy levels for Li atoms. The arrows indicate the dipole-allowed transitions.

$$\delta = \sum_{j > i} N_j A_{ji} \kappa_{ji} + N_e \left( \sum_{j > i} N_j R_{ji} + N^+ N_e \beta_{ci} \right) - N_e N_i \left( \sum_{j > i} C_{ij} + S_{ic} \right). \quad (4)$$

The magnitude  $\delta$  can be neglected in Eq. (3) in many plasmas with medium and high electron density ( $> 10^{12} \text{ cm}^{-3}$ ) because in such a case I have that

$$N_e \sum_{j < i} N_j C_{ji} \gg \delta. \quad (5)$$

If I neglect the quantity  $\delta$ , the concentrations of the Li atoms excited to the  $i$ th energy level (with  $i = 2, 3, 4, 5$ ) can be obtained from the analytic expression

$$N_i = \frac{N_e \sum_{j < i} N_j C_{ji}}{\sum_{j < i} A_{ij} \kappa_{ij} + N_e \sum_{j < i} R_{ij}}, \quad (6)$$

where only rate coefficients for collisional electronic excitations and deexcitations, and spontaneous emission are required. Taking into account the earlier considerations, the population densities of the excited Li atomic levels can be given in Boltzmann-like form

TABLE I. Transition probabilities  $A_{ji}$  (in  $10^7 \text{ s}^{-1}$ ) and corresponding wavelengths  $\lambda_{ji}$  (in nm) for dipole-allowed transitions between the lower electronic levels of lithium atoms.

| $j \rightarrow i$ | Transition              | $A_{ji} (10^7 \text{ s}^{-1})$ | $\lambda_{ji} \text{ (nm)}$ |
|-------------------|-------------------------|--------------------------------|-----------------------------|
| $2 \rightarrow 1$ | $2^2P \rightarrow 2^2S$ | 3.720                          | 670.8                       |
| $3 \rightarrow 2$ | $3^2S \rightarrow 2^2P$ | 3.490                          | 812.6                       |
| $4 \rightarrow 1$ | $3^2P \rightarrow 2^2S$ | 0.117                          | 323.2                       |
| $4 \rightarrow 3$ | $3^2P \rightarrow 3^2S$ | 0.377                          | 2687.7                      |
| $5 \rightarrow 2$ | $3^2D \rightarrow 2^2P$ | 7.160                          | 610.3                       |
| $5 \rightarrow 4$ | $3^2D \rightarrow 3^2P$ | 0.000 381                      | 27 949.0                    |

TABLE II. Relaxation times (in s) for the  $i=2, 3, 4, 5$  levels of atomic lithium assuming  $T_e=0.70$  and  $T_e=0.75$  eV.

| $T_e$ (eV) | $N_e$ (cm <sup>-3</sup> ) | $i=2$                 | $i=3$                 | $i=4$                 | $i=5$                 |
|------------|---------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 0.7        | $1.0 \times 10^{16}$      | $1.1 \times 10^{-9}$  | $4.5 \times 10^{-11}$ | $3.3 \times 10^{-13}$ | $4.4 \times 10^{-13}$ |
|            | $2.0 \times 10^{16}$      | $5.7 \times 10^{-10}$ | $2.3 \times 10^{-11}$ | $1.6 \times 10^{-13}$ | $2.2 \times 10^{-13}$ |
|            | $3.0 \times 10^{16}$      | $3.8 \times 10^{-10}$ | $1.5 \times 10^{-11}$ | $1.1 \times 10^{-13}$ | $1.5 \times 10^{-13}$ |
|            | $4.0 \times 10^{16}$      | $2.9 \times 10^{-10}$ | $1.1 \times 10^{-11}$ | $8.3 \times 10^{-14}$ | $1.1 \times 10^{-13}$ |
|            | $5.0 \times 10^{16}$      | $2.3 \times 10^{-10}$ | $9.1 \times 10^{-12}$ | $6.6 \times 10^{-14}$ | $8.9 \times 10^{-14}$ |
| 0.75       | $1.0 \times 10^{16}$      | $1.0 \times 10^{-9}$  | $4.3 \times 10^{-11}$ | $3.2 \times 10^{-13}$ | $4.4 \times 10^{-13}$ |
|            | $2.0 \times 10^{16}$      | $5.1 \times 10^{-10}$ | $2.1 \times 10^{-11}$ | $1.6 \times 10^{-13}$ | $2.2 \times 10^{-13}$ |
|            | $3.0 \times 10^{16}$      | $3.4 \times 10^{-10}$ | $1.4 \times 10^{-11}$ | $1.1 \times 10^{-13}$ | $1.4 \times 10^{-13}$ |
|            | $4.0 \times 10^{16}$      | $2.6 \times 10^{-10}$ | $1.1 \times 10^{-11}$ | $8.0 \times 10^{-14}$ | $1.1 \times 10^{-13}$ |
|            | $5.0 \times 10^{16}$      | $2.0 \times 10^{-10}$ | $8.6 \times 10^{-12}$ | $6.4 \times 10^{-14}$ | $8.7 \times 10^{-14}$ |

$$\left(\frac{N_j}{N_i}\right)_{\text{neq}} = \frac{B_j}{B_i} \left(\frac{N_j}{N_i}\right)_{\text{eq}}, \quad (7)$$

with

$$\left(\frac{N_j}{N_i}\right)_{\text{eq}} = f_{ji} = \frac{\omega_j}{\omega_i} \exp\left(-\frac{E_j - E_i}{kT_e}\right), \quad (8)$$

where  $E_i$  and  $E_j$  are the energies of the levels (relative to the ground state), and  $\omega_j$  and  $\omega_i$  are statistical weights of the levels. The coefficients  $B_i$  measure the deviation of each of the  $i$ th excited state of Li atoms present in the plasma from their corresponding thermodynamic equilibrium concentration, and are given by

$$B_i = \frac{\sum_{j<i} B_j \tau_{ij}}{1 + \sum_{j<i} \tau_{ij}} \quad \text{with} \quad \tau_{ij} = \frac{N_e R_{ij}}{\sum_{j<i} A_{ij} \kappa_{ij}}, \quad (9)$$

with  $B_1 = 1$ .

Therefore, according to before, Eqs. (7)–(9) are enough to calculate the concentration of the excited Li atomic levels  $i=2, 3, 4$ , and  $5$ . In order to derive the concentration of Li atoms in their ground level ( $i=1$ ), one just needs to solve Eq. (2) for steady-state plasmas. After some calculations I reach

$$N_1 = \frac{N_e^2 \beta_{c1}}{S_{1c}} \text{ cm}^{-3}. \quad (10)$$

When the population of an atomic Li level departs (as a result of a small change of plasma parameters) from its steady-state value, then some time (called the relaxation time) is needed to reestablish the steady-state population of the level. The relaxation times for each atomic level (including the ground) of Li can be calculated as<sup>9</sup>

$$\tau_i = \left\{ \sum_{k<i} (N_e R_{ik} + A_{ik}) + \sum_{j>i} \left[ N_e C_{ij} + \frac{N_j}{N_i} (1 - \kappa_{ji}) A_{ji} \right] + N_e S_{ic} \right\}^{-1} \text{ s}, \quad (11)$$

where ionizing collisions are only taken into account from the ground atomic level, that is, we assume that  $S_{ic}=0$  (for  $i=2, 3, 4$ , and  $5$ ).

The laser-produced plasmas that concern me in this work are not stationary but rather in transient conditions. Therefore, in order to study the kinetics of a transient plasma with a stationary kinetic model I first need to evaluate the time scales of the different processes involved. These transients are, in general, much longer than the relaxation times of the different excited levels of Li atoms (see Table II) but, often, they are shorter than the relaxation time of ground state Li. However, for plasmas produced by lasers with a pulse duration of several nanoseconds, it happens to be that the relaxation times of electrons<sup>10</sup> (the thermalization time) is much shorter than any characteristic time scale of the laser-produced plasma. Consequently, the time-dependent rate equations for calculating the concentration of the electrons in the transient plasmas of interest here can be solved by assuming that electrons are in steady state. Therefore, I can study the kinetics driven by electrons in our plasma by applying the steady-state collisional-radiative model used in this work not only to levels  $i=2, 3, 4$ , and  $5$  but also to the case of the ground state since the concentration of the latter one can be obtained from the rate equation for the plasma electrons.

Concerning rate coefficients for the electron-impact excitation and deexcitation processes, I use here the collisional rate coefficients proposed by Kunc and Zgorzelski<sup>4</sup> for alkali metal atoms based on the classical binary-encounter theory by Gryzinski.<sup>5</sup> The rate coefficient  $C_{ij}$  for an electron-impact excitation of a lithium atom from a lower level  $i$  to an upper level  $j$  is expressed by the averaged (assuming Maxwellian electron energy distribution) collisional rate coefficient  $C_{ij}$  given by

$$C_{ij} = 2 \left( \frac{2}{\pi m_e} \right)^{1/2} \left( \frac{1}{kT_e} \right)^{3/2} \int_0^\infty \sigma_{ij}(\epsilon) \times \epsilon e^{-\epsilon/kT_e} d\epsilon \text{ cm}^3 \text{ s}^{-1}, \quad (12)$$

where  $m_e$  and  $e$  are the electron mass and electron charge, respectively and  $T_e$  denotes the free-electron temperature,  $k$  is the Boltzmann constant, and  $\sigma_{ij}(\epsilon)$  stands for the cross section for electron collisional excitation from level  $i$  to level  $j$ .

On the other hand, the principle of detailed balance allows me to calculate the electron-impact deexcitation rate coefficients  $R_{ji}$  as

$$R_{ji} = \frac{\omega_i}{\omega_j} \exp(y_{ij}) C_{ij} \quad \text{cm}^3 \text{s}^{-1}, \quad (13)$$

with  $\omega_i = 2l_i + 1$  ( $l_i$  is the angular-momentum quantum number of level  $i$ ) and  $y_{ij} = (E_j - E_i)/kT_e$ .

The electron-impact ionization rate coefficient from the ground level of lithium is taken from Drawin<sup>11</sup> and it can be written in an analytic form like

$$S_{1c} = 1.46 \times 10^{-10} \zeta_1 \left( \frac{I_H}{I_1} \right)^2 T_e^{1/2} (K) \times u_1 \Psi_1(u_1, \chi_1) \quad \text{cm}^3 \text{s}^{-1}, \quad (14)$$

with  $\zeta_1 = 1$ , and  $I_1 = 5.4 \text{ eV}$  and  $I_H = 13.56 \text{ eV}$  being the ionization energy of the ground level of atomic lithium and of the hydrogen atom, respectively,  $u_1 = I_1/kT_e$  and  $\chi_1 = 1 + (Z_{\text{eff}} - 1)/(Z_{\text{eff}} + 2)$  so that  $\chi_1 = 1$  ( $Z_{\text{eff}} = 1$ ), where  $Z$  and  $Z_{\text{eff}} = Z - N + 1$  are the atomic number and the effective atomic number (with  $N$  being the number of bound electrons in lithium). The function  $\Psi_1$  is taken from Drawin and it also admits an approximate analytic expression like<sup>11</sup>

$$\Psi_1(u_1, \chi_1 = 1) \cong \left( \frac{e^{-u_1}}{1 + u_1} \right) \left\{ \frac{1}{20 + u_1} + \ln \left[ 1.25 \left( 1 + \frac{1}{u_1} \right) \right] \right\}. \quad (15)$$

Taking into account the principle of detailed balance, we can derive the three-body electron recombination rate coefficient as<sup>9</sup>

$$\beta_{c1} = 3.32 \times 10^{-22} \left( \frac{1}{kT_e} \right)^{3/2} \exp(I_1/kT_e) S_{1c} \quad \text{cm}^6 \text{s}^{-1}. \quad (16)$$

I now proceed to define the coefficients that will allow me to evaluate the relative contribution of the different kinetic mechanisms considered for populating and depopulating the ground and excited energy levels of Li atoms. I have that the total loss ( $L_i$ ) and gain ( $G_i$ ) coefficients for the ground ( $i=1$ ) and excited ( $2 \leq i \leq 5$ ) energy levels taken into account here are given by

$$L_1 = \sum_{j=2}^5 C_{1j} + S_{1c} \quad \text{and} \quad G_1 = \sum_{j=2}^5 R_{j1} + N_e \beta_{c1} \quad (17)$$

and

$$L_i = \sum_{j=i+1}^5 C_{ij} + \sum_{j=1}^{i-1} R_{ij} \quad \text{and} \quad G_i = \sum_{j=i+1}^5 R_{ji} + \sum_{j=1}^{i-1} C_{ji} \quad \text{with} \quad 2 \leq i \leq 5. \quad (18)$$

Therefore, the relative loss ( $l_{1c}$ ) and gain ( $g_{c1}$ ) coefficients for the ground energy level ( $i=1$ ) due to, respectively, electronic ionization to the continuum ( $c$ ) and three-body collisional recombination from the continuum, are

$$l_{1c} = \frac{S_{1c}}{L_1} \quad \text{and} \quad g_{c1} = \frac{N_e \beta_{c1}}{G_1} \quad (19)$$

and the relative loss ( $l_{ij}$ ) of level  $i$ , due to electron collisional excitations and/or deexcitations, to a level  $j$  is given by

$$l_{ij} = \frac{C_{ij}}{L_i} \quad \text{with} \quad 1 \leq i < j \leq 5 \quad \text{or} \quad l_{ij} = \frac{R_{ij}}{L_i} \quad \text{with} \quad 5 \geq i > j \geq 1, \quad (20)$$

while the relative gain ( $g_{ji}$ ) of level  $i$ , due to electron collisional deexcitation and/or excitations, from a level  $j$  is given by

$$g_{ji} = \frac{R_{ji}}{G_i} \quad \text{with} \quad 1 \leq i < j \leq 5 \quad \text{or} \quad g_{ji} = \frac{C_{ji}}{G_i} \quad \text{with} \quad 5 \geq i > j \geq 1. \quad (21)$$

It is interesting to note that all the earlier coefficients, except  $G_1$  and  $g_{c1}$ , are only electron temperature dependent while the dependence of  $G_1$  and  $g_{c1}$  on the electron temperature is very weak.

### III. MEASUREMENT OF THE CONCENTRATION OF LITHIUM ATOMS

In order to evaluate the experimental Li atom concentration present in the plasma formed by ablation of a LiNbO<sub>3</sub> target by means of an ArF laser (193 nm and 20 ns of pulse width), I have used measurements, obtained by optical (atomic) absorption spectroscopy, of the temporal evolution of the optical density associated to the Li 670.8 nm resonance absorption transition at 11 mm from the LiNbO<sub>3</sub> target and with a laser fluence of 0.06 J cm<sup>-2</sup> (absorption experiments are very difficult at higher fluences). In addition, by performing optical (atomic) emission spectroscopy as in Ref. 12, I have obtained the temporal behavior (at 11 mm from the target) of the full width at half maximum (FWHM),  $\Delta\lambda_{1/2}^{2 \rightarrow 1}$ , of the emission line 670.8 nm corresponding to the transition from the excited level  $j=2$  to the ground level  $i=1$  of Li atoms. These latter emission experiments were carried out at a laser fluence of 1.2 J cm<sup>-2</sup> since no emission could be observed at 0.06 J cm<sup>-2</sup>; I found that  $\Delta\lambda_{1/2}^{2 \rightarrow 1}$  ( $L=11 \text{ mm}$ )  $\cong 0.79 \text{ \AA}$  for times greater than 1  $\mu\text{s}$ . Therefore, in order to have an approximate value for  $N_{\text{Li}(i=1)}^{\text{Exp}}(t)$  from Eq. (27) (see later), I have assumed that  $\Delta\lambda_{1/2}^{1 \rightarrow 2} \cong \Delta\lambda_{1/2}^{2 \rightarrow 1}$  and that  $\Delta\lambda_{1/2}^{2 \rightarrow 1}(0.06 \text{ J cm}^{-2}) \sim \Delta\lambda_{1/2}^{2 \rightarrow 1}(1.2 \text{ J cm}^{-2})$ .

Following the earlier assumptions, I now derive an expression that allows me to approximately deduce and quantify, from optical (atomic) absorption and emission measurements, the experimental temporal evolution of the ground state Li atom concentration present in the plasma formed in my PLD system.

The absorption of radiation in a plasma can be evaluated through the Lambert–Beers law relating the incident light intensity  $I_0^\lambda$ , at a certain wavelength  $\lambda$  and passing through an absorbing medium (plasma) with absorption coefficient  $\eta_\lambda$  and length  $L$ , with the outcoming light intensity  $I_L^\lambda$ . Therefore<sup>13</sup>



$$I_L^\lambda = I_0^\lambda e^{-\eta_\lambda L} \quad \text{with} \quad \eta_\lambda = \sum_i N_i \sigma_{\lambda,i} \text{ cm}^{-1}, \quad (22)$$

where  $N_i$  and  $\sigma_{\lambda,i}$  stand for the population density of those species in the plasma capable of absorbing radiation and their absorption cross section, respectively. Depending on the wavelength of the incident light, several absorption mechanisms can contribute to quantify the absorption coefficient. In my case, I have used optical absorption measurements from experiments that used a lithium hollow-cathode lamp to measure the Li atomic absorption at the 670.8 nm unresolved resonance doublet ( $i=1 \rightarrow j=2$  or  $2s^2S_{1/2} \rightarrow 2p^2P_{1/2}^0$ )<sup>14</sup> and at a distance of 11 mm from the target. Therefore, the Li resonance absorption mechanism at 670.8 nm prevails above others since the energy ( $\sim 1.9$  eV) associated to the incident radiation of that transition,  $I_0^{\lambda(1 \rightarrow 2)}$ , as well as its low intensity are not enough for promoting other absorption processes like atomic photoionization events (from the ground or excited states of Li atoms) that might be common in absence of molecular species in the plasma. Now, I can easily derive from Eq. (22) a general approximate expression for the experimentally obtained concentration of ground state lithium atoms like

$$N_{\text{Li}(i=1)}^{\text{Exp}} = \frac{2.3026}{\sigma_{1 \rightarrow 2} L} \log(I_0^{\lambda_{12}}/I_L^{\lambda_{12}}) \text{ cm}^{-3}, \quad (23)$$

with the cross section for the bound-bound absorption corresponding to the atomic transition from the ground level  $i=1$  to the level  $j=2$  being given by<sup>15</sup>

$$\sigma_{1 \rightarrow 2} = \frac{r_e c}{4 \epsilon_0} f_{1 \rightarrow 2} \phi_{1 \rightarrow 2}(\nu) \text{ cm}^2, \quad (24)$$

where  $\log(I_0^\lambda/I_L^\lambda)$  is the optical density,  $r_e = 2.818 \times 10^{-13}$  cm is the classical electron radius,  $c$  is the speed of light in vacuum,  $\epsilon_0 = 1$  is the permittivity of free space,  $f_{1 \rightarrow 2} = 0.753$  is the absorption oscillator strength for the 670.8 nm transition,  $\nu$  is the light frequency and  $\phi_{1 \rightarrow 2}(\nu)$  is the absorption line shape factor for the  $i=1 \rightarrow j=2$  transition (670.8 nm) in atomic lithium. Under the experimental conditions of laser ablation for film deposition (where relatively high electron densities are usually measured), the Stark effect is the main line broadening mechanism contributing to the absorption line shape factor which is given by a Lorentzian-like function,<sup>15</sup>

$$\begin{aligned} \phi_{1 \rightarrow 2}(\nu) &= \frac{1}{\pi} \frac{\Delta \nu^{1 \rightarrow 2} \Delta \lambda^{1 \rightarrow 2}_{1/2}/2}{(\nu - \nu_{12})^2 + (\Delta \nu^{1 \rightarrow 2} \Delta \lambda^{1 \rightarrow 2}_{1/2})^2} \\ &\cong \phi_{1 \rightarrow 2}(\nu = \nu_{12}) = \frac{2}{\pi \Delta \nu^{1 \rightarrow 2} \Delta \lambda^{1 \rightarrow 2}_{1/2}} \text{ s}, \end{aligned} \quad (25)$$

where  $\Delta \nu^{1 \rightarrow 2}_{\Delta \lambda_{1/2}}$  is related with  $\Delta \lambda^{1 \rightarrow 2}_{1/2}$ , the FWHM, by the expression

$$\Delta \nu^{1 \rightarrow 2}_{\Delta \lambda_{1/2}} = \Delta \lambda^{1 \rightarrow 2}_{1/2} \frac{c}{\lambda_{12}^2} \text{ s}^{-1}, \quad (26)$$

and, therefore, I finally reach an approximate expression for the temporal evolution of the experimental concentration of ground state lithium atoms at a certain distance from the

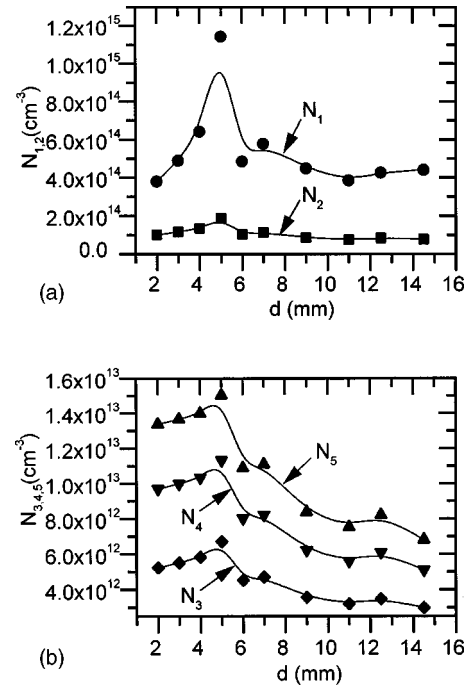


FIG. 2. Predicted population densities for Li atoms in their (a) ground,  $N_1$  (●), and first excited level,  $N_2$  (■), and (b) upper excited levels,  $N_3$  (◆),  $N_4$  (▼), and  $N_5$  (▲), as a function of the distance from the target. The laser fluence is  $1.2 \text{ J cm}^{-2}$ . The solid lines are the best fits.

target in terms of the optical density and the Stark broadening of the transition line selected, that is, in terms of two magnitudes that can be easily measured at the laboratory

$$N_{\text{Li}(i=1)}^{\text{Exp}}(t) \cong \frac{2.3026 \times \Delta \lambda_{1/2}^{1 \rightarrow 2}}{L \times 1.52 \times 10^{-14}} \log \left[ \frac{I_0^{\lambda_{12}}}{I_L^{\lambda_{12}}(t)} \right] \text{ cm}^{-3}. \quad (27)$$

#### IV. RESULTS AND DISCUSSION

In this section we will describe and discuss the main predictions from the kinetic model as well as their comparison with the experimental results available from studies of the plasma produced by laser ablation of  $\text{LiNbO}_3$  targets in vacuum.

Figures 2(a) and 2(b) show, respectively, the predicted spatial evolution (at a laser fluence of  $1.2 \text{ J cm}^{-2}$ ) of the concentrations of the ground and first excited energy level, and that of excited levels  $i=3$  to  $i=5$  of Li. The more remarkable features in Fig. 2 are the presence of a maximum at around 5 mm from the target and the fact that the concentrations of levels  $i=3$ ,  $i=4$ , and  $i=5$  are inverted, that is,  $N_5 > N_4 > N_3$ . The latter happens since, according to my model, the ratio  $\gamma_i = G_i/L_i$  (balance between gain,  $G_i$ , and loss,  $L_i$ , mechanisms for a particular level  $i$ ) remains constant for any distance from the target for the five energy levels considered and it is higher for  $i=5$  ( $\gamma_5 = 1.33$ ) and  $i=4$  ( $\gamma_4 = 0.75$ ) than for  $i=3$  ( $\gamma_3 = 0.36$ ). The constant values of  $\gamma_i$  are directly connected to the fact that the available spatial and temporal measurements of the electron temperature in the plasma formed during PLD experiments in vacuum of  $\text{LiNbO}_3$  were mostly constant.<sup>12</sup> In addition, while the populations of the ground and first excited level of Li atoms are almost constant

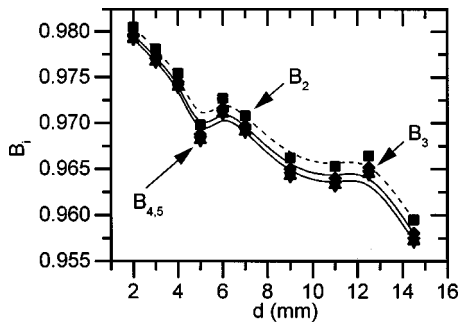


FIG. 3. Coefficients  $B_i$  measuring the deviation of the first excited level,  $i=2$  (■), and upper excited levels,  $i=3$  (◆), 4 (▼), 5 (▲), of Li atoms from thermal equilibrium as a function of the distance from the target. The solid lines are the best fits.

from a distance of roughly 7 mm to the last considered distance (15 mm), those of levels  $i=3$ ,  $i=4$ , and  $i=5$  keep decreasing beyond 7 mm.

The coefficients  $B_i$  accounting for the deviation of the population density of Li atoms in the plasma from the local thermodynamic equilibrium (LTE), are plotted in Fig. 3 as a function of the distance from the target. Since  $B_i=1$  when LTE occurs, these results show that when working with a laser fluence of  $1.2 \text{ J cm}^{-2}$ , the laser generated plasma almost preserves LTE as I go away from the target. Moreover, the lower the energy level, the closer it is to its LTE concentration value.

I now proceed to discuss the time evolution of the concentration of the five energy levels considered for Li atoms.

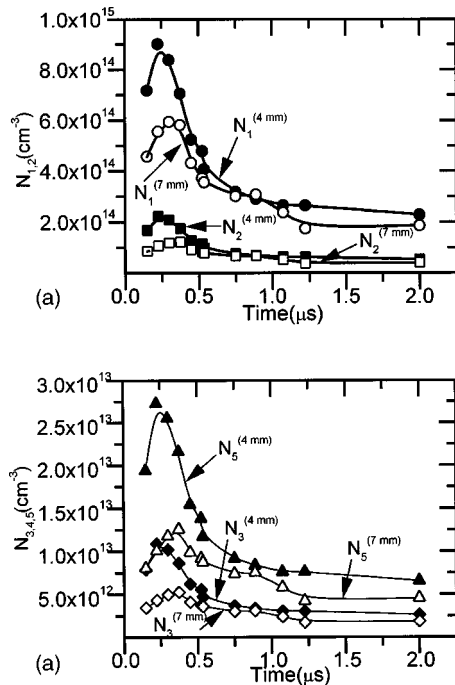


FIG. 4. Predicted population densities for Li atoms in their (a) ground,  $N_1$  (●), and first excited level,  $N_2$  (■), and (b) upper excited levels,  $N_3$  (◆),  $N_4$  (▼), and  $N_5$  (▲), as a function of the time after the laser pulse is off and for two distances from the target:  $L=4 \text{ mm}$  (solid symbol) and  $L=7 \text{ mm}$  (open symbol). The laser fluence is  $1.2 \text{ J cm}^{-2}$ . The solid lines are the best fits.

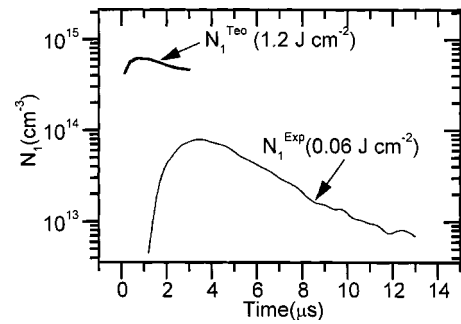


FIG. 5. Comparison between the theoretically predicted ( $N_1^{\text{Teo}}$ ) temporal evolution, at a laser fluence of  $1.2 \text{ J cm}^{-2}$ , of the population density of the ground energy level of Li atoms, and the experimental values of  $N_1^{\text{Exp}}$  (at  $0.06 \text{ J cm}^{-2}$ ) from expression (27). The distance from the target is  $L=11 \text{ mm}$ . The solid lines are the best fits.

Figures 4(a) and 4(b) show, respectively, the predicted temporal evolution of the concentrations of the ground and first excited energy level [Fig. 4(a)], and that of the excited levels  $i=3$  and  $i=5$  [Fig. 4(b)]. The most remarkable feature in Figs. 4(a) and 4(b) is the presence, as in the spatial evolution, of a maximum. This maximum shifts to longer times as I separate from the target:  $\sim 0.25 \mu\text{s}$  (at 4 mm),  $\sim 0.37 \mu\text{s}$  (at 7 mm), and  $\sim 0.75 \mu\text{s}$  (at 11 mm, see Fig. 5). It is also interesting to note that the population densities of all levels become constant at around 0.75 and  $1\text{--}1.2 \mu\text{s}$  at, respectively, 4 and 7 mm from the target.

A qualitative agreement is found when comparing the predicted time evolution of  $N_1$  in Fig. 4(a) for ArF laser ablation (at  $\sim 1.2 \text{ J cm}^{-2}$ ) of LiNbO<sub>3</sub> targets with the experimental  $N_1$  values of Harnafi and Dubreuil<sup>16</sup> obtained by using laser-induced fluorescence spectroscopy at 5 and 7 mm from the target and after CO<sub>2</sub> laser ablation (at  $\sim 0.8 \text{ J cm}^{-2}$ ) of a solid lithium target in vacuum. However, a more precise (quantitative) comparison is hardly possible not only because different targets are used but also because of the different ablation mechanisms involved when using a CO<sub>2</sub> or an ArF laser.

In Fig. 5 we present a comparison, at a distance of 11 mm from the target, between the theoretical temporal evolution of the population density of the ground energy level of Li ( $N_1^{\text{Teo}}$ ) predicted by the kinetic model (at a laser fluence of

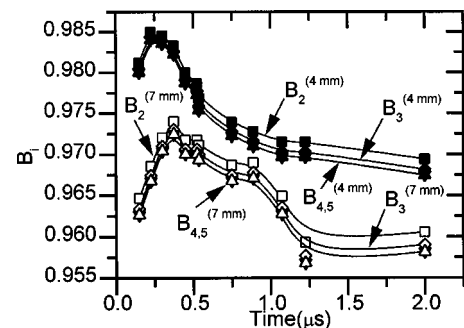


FIG. 6. Coefficients  $B_i$  measuring the deviation of the first excited level,  $i=2$  (■), and upper excited levels,  $i=3$  (◆), 4 (▼), 5 (▲), of Li atoms from thermal equilibrium as a function of the time after the laser pulse is off and for two distances from the target:  $L=4 \text{ mm}$  (solid symbol) and  $L=7 \text{ mm}$  (open symbol). The solid lines are the best fits.

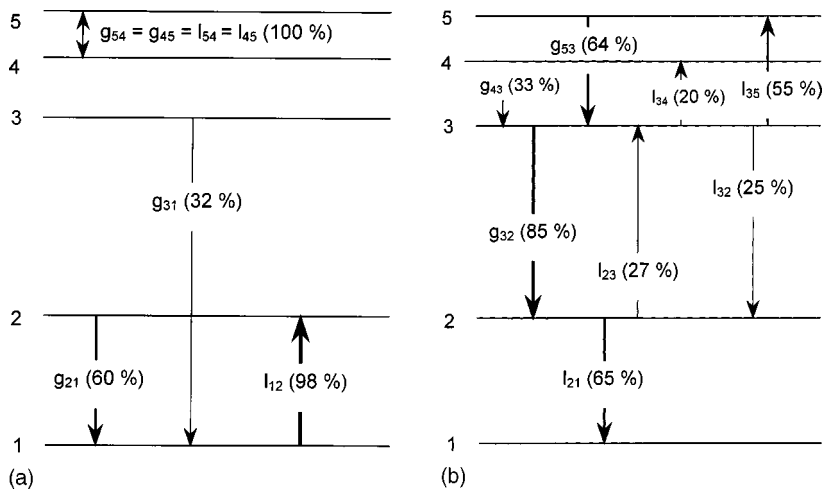


FIG. 7. Most relevant electron-impact kinetic mechanisms responsible for (a) populating ( $g_{j,i}$ ) and depopulating ( $l_{i,j}$ ) levels  $i=1, 4, 5$ , and (b) populating ( $g_{j,i}$ ) and depopulating ( $l_{i,j}$ ) levels  $i=2, 3$  of Li atoms in the laser-generated plasma after ablation of a LiNbO<sub>3</sub> target in vacuum.

$1.2 \text{ J cm}^{-2}$ ) and the experimental values of  $N_1^{\text{Exp}}$  (at  $0.06 \text{ J cm}^{-2}$ ) obtained from Eq. (27) using the experimentally measured optical (atomic) absorption transients (at the 670.8 nm resonance line of Li I) in the laser-generated plasma after ablation of LiNbO<sub>3</sub> targets. I see that there is a fairly good qualitative agreement between  $N_1^{\text{Teo}}(1.2 \text{ J cm}^{-2})$  and  $N_1^{\text{Exp}}(0.06 \text{ J cm}^{-2})$ , being the most significant different the fact that the maximum observed at both energies happens faster (as it is expected) at  $1.2 \text{ J cm}^{-2}$  than at  $0.06 \text{ J cm}^{-2}$ .

The coefficients  $B_i$  are represented in Fig. 6 as a function of the time after the laser pulse is off and for two distances (4 and 7 mm) from the target. I see that the closer to the target, the smaller the deviation of the plasma from LTE and, in general, the lower the energy level, the closer it is to its LTE concentration value.

Finally, I have obtained that both the relative loss,  $l_{ij}$  [Eq. (20)], and gain rate coefficients,  $g_{ji}$  [Eq. (21)] remain constant as I go away from the target for any time interval after the laser pulse is off. Figure 7 represents the partial contribution of each of these rate coefficients to the population and depopulation of the considered energy levels of Li atoms. As can be seen in Fig. 7(a), the collisional excitation and deexcitation processes from, respectively, level 4–5, and 5–4 are the same and they are the most important for populating and depopulating these two upper energy levels. In addition, whereas collisional deexcitation mechanisms from levels 2 (~60%) and 3 (~32%) are responsible for populating the ground level of Li atoms, collisional excitation (~98%) from level 1 to level 2 is the main mechanism for depopulating the ground level. Regarding Fig. 7(b), I see that collisional deexcitation from levels 4 (~33%) and 5 (~64%) are the principal populating mechanisms of level 3, while collisional excitation to levels 4 (~20%) and 5 (~55%) together with deexcitation processes to level 2 (~25%) are the most important depopulating mechanisms of level 3. Moreover, the collisional deexcitation (~85%) from level 3 is the principal populating process for level 2, while its collisional decay (~65%) to the ground level and collisional excitation (~25%) to level 3 are the main kinetic mechanisms depopulating level 2.

## V. SUMMARY AND CONCLUSIONS

In this work, I have studied the spatial and temporal electron kinetics of the nonequilibrium plasma generated by laser ablation of LiNbO<sub>3</sub> targets in vacuum. A very convenient analytic quasistationary kinetic model for studying the laser-generated plasma has allowed me to predict the spatial and temporal behavior of the ground ( $N_1^{\text{Teo}}$ ) and excited level concentrations of Li atoms, as well as the underlying electron collisional excitation and deexcitation mechanisms leading to the predicted Li population densities and their possible deviation from LTE. The model considered here uses as input parameters the experimental values of the  $N_e$  and  $T_e$  obtained from optical (atomic) emission measurements. In addition, we have also developed an analytic procedure that allows one to determine the experimental concentration ( $N_1^{\text{Exp}}$ ) of ground Li atoms from optical (atomic) absorption measurements.

Therefore, a significant advantage of the approach used in this work is that it allows us to not only to compare theoretical predictions with available experimental results but it also provides physical insight on the possible kinetic mechanisms controlling the Li atom population densities obtained. I found that the laser-generated plasma is almost in LTE and that, in general, the qualitative agreement between  $N_1^{\text{Teo}}$  and  $N_1^{\text{Exp}}$  is quite reasonable, even at the quantitative level.

In summary, the present approach can be employed as a useful general diagnostic tool for estimating atom population densities in those plasmas produced in the pulsed laser ablation of solid targets used for deposition of thin solid films.

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